

INVESTIGATION OF LOW-RANK COAL HYDROLYSIS

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INTRODUCTION

Recently, increased attention is being directed toward the pyrolysis route of processing coal to produce liquid and gaseous fuels, in particular when coupled with the use of char by-product for power generation.(1) In view of the increased interest in coal pyrolysis, a better understanding of the thermal response of coals as they are heated under various conditions is needed.

Conventional liquefaction processes developed for Eastern bituminous coals might not be the best choice for Western low-rank coals because of the substantial property and structural differences between them. In general, low-rank coals are more susceptible to reaction with H_2 , CO , or H_2S .

Coal hydrolysis is defined as pyrolysis under hydrogen pressure and involves the thermal decomposition of coal macerals followed by evolution and cracking of volatiles in the hydrogen. It is generally agreed that the presence of hydrogen during the pyrolysis increases overall coal conversion.(2,3)

In the present study we investigated pyrolysis of various ranks of coals under different gaseous environments. Low-rank coals such as Wyoming subbituminous coal and North Dakota lignite were pyrolyzed and their results were compared with Kentucky and Illinois bituminous coals.

EXPERIMENTAL

The coals used in this study included Wyoming subbituminous coal, North Dakota lignite, Kentucky bituminous coal, and Illinois No. 6 bituminous coal. Proximate and ultimate analyses of the coals studied are given in Table I.

All pyrolysis experiments were carried out in the thermogravimetric apparatus (TGA) having a pressure capacity of up to 1000 psi. A schematic of the experimental unit is shown in Figure 1. It consists of the DuPont 1090 Thermal Analyzer and the micro-balance reactor. The latter was enclosed inside a pressure vessel with a controlled temperature programmer and a computer data storage system. The pressure vessel was custom manufactured by Autoclave Engineers. A similar set-up was used previously by others.(4) A chromel-alumel thermocouple was set in close proximity to the sample inside a reactor. The reactor was made of a quartz tube which was surrounded by a tubular furnace. In a typical coal pyrolysis run, the coal sample (20-30 mg) was placed in a platinum boat which was suspended from the quartz beam of the TGA balance. The coal particle size used was 100-200 mesh. Samples were heated to desired temperatures at linear heating rates or heated isothermally under various gaseous environments.

FT-infrared was also used to monitor the degree of pyrolysis for various samples at different temperatures. The KBr (potassium bromide) pellet of sample was prepared for FTIR analysis.

RESULTS AND DISCUSSION

Typical thermograms of Wyoming coal under hydrogen pressure are given in Figure 2. The TGA and the weight loss rate thermograms show a major weight loss at temperatures ranging from 350-600°C. A secondary hydrolysis peak occurs above 600°C most likely due to the gas releases from the further decomposition of coal.

Figure 3 shows a comparison of derivative thermograms for four different rank coals. The differences of devolatilization rate are not large at temperatures up to 500°C, however, above 500°C, the secondary hydropyrolysis peak of low-rank coal becomes dominant.

The influence of heating rate on coal hydropyrolysis was studied over a range of 5-100°C/min. As shown in Figure 4, the two peaks were observed, the first of which we call the primary volatilization, and the second, characteristic of local hydropyrolysis. The first peak increased rapidly with the increase of the heating rate. The second characteristic peak becomes relatively dominant at lower heating rates. It seems that the hydropyrolysis peak is favored by slow heating rates, indicating a heat transfer limitation within the secondary hydropyrolysis region. In contrast, coal pyrolyzed under an inert nitrogen atmosphere results in an increase of weight loss rate with increasing heating rates, but the shape of the curves remains the same (Figure 5).

The effect of hydrogen on coal pyrolysis can further be illustrated by Figure 6, where we compared derivative thermograms of Wyoming coal pyrolyzed at 200 psig of N₂ and 200 psig of H₂ at the same heating rates (20°C/min). The secondary hydropyrolysis peak observed at 580°C in the H₂ run was absent in the N₂ atmosphere.

FTIR spectra of the original coal and char from pyrolyzing Wyoming coal under H₂ pressure at various temperatures are shown in Figure 7 (only wave numbers between 1700 and 400 cm⁻¹ were shown here for comparison). The strongest absorption band located at 1600 cm⁻¹ begins to decrease in intensity at 470°C. This band has been assigned to aromatic ring C-C vibration associated with phenolic/phenoxy groups.(5) Similarly, the aromatic-oxygen vibration band near 1260 cm⁻¹ shows an equivalent decrease. The absorption bands between 720 to 870 cm⁻¹ (which arise from the out-of-plane aromatic CH vibrations) increase markedly at 470°C, indicating a growth in size of aromatic clusters in the reacted coal. At 650°C, most organic absorption bands were diminished except for a broad band ranging from 1000-1090 cm⁻¹ due to clay mineral absorption.(7) An increase in the structureless background absorption is observed, suggesting a growth of graphitization in the residue coal.

The kinetics of coal pyrolysis are complicated because of the numerous components or species which are simultaneously pyrolyzed and decomposed. For measuring kinetic parameters, we treated data following the procedure of Coats and Redfern (8) and Mickelson and Einhorn.(9) The kinetic parameters for four different coals heated under H₂ pressure are presented in Table II. A reaction order equal 2.3 to 2.9 was observed for the primary hydropyrolysis peaks. A high reaction order was obtained for the secondary reaction peak under hydrogen pressure. The kinetic parameters for four different coals heated under N₂ atmosphere compared with data presented in the literature are listed in Table III.

Kinetic parameters for *n* (reaction order) and *E* (activation energy) in the literature show significant variation for different techniques and coal (Table III). By considering the complexity of coal thermal degradation, many authors have contended that a simple, first-order reaction is inadequate. Wiser et al. (10) found that *n*=2 gave the best fit to their data, while Skylar et al. (11) observed that values of *n* above 2 were required to fit nonisothermal devolatilization data for different coals. The kinetic parameters obtained in this study also show a non-integer reaction order. The thermal decomposition of coals are complex because of the numerous components or species which are simultaneously decomposed and recondensed.

Figure 8 demonstrates the influence of CO on devolatilization for different ranks of coal. For the higher rank coals (i.e., Kentucky and Illinois bituminous coals), pyrolysis in the presence of CO plus H₂ or H₂ alone follows the

same path. However, lignite showed a marked increase of pyrolysis rate in the run where CO was added. A higher content of reactive oxygenated bonds (i.e., carboxyl or ether linkages) in low-rank coals could be the reason for the high reactivity in the presence of CO. The kinetic parameters determined for coal pyrolyzed in syngas (CO/H₂ mixture) are listed in Table IV. As shown in the table, a high reaction order was obtained for the H₂ and CO/H₂ runs, particularly for the low-rank coals which showed a secondary reaction occurring at temperatures above 500°C.

CONCLUSIONS

Laboratory microscale studies have demonstrated that the coal pyrolysis in a hydrogen atmosphere gave higher degree of devolatilization in low-rank coals than pyrolysis in an inert atmosphere. In hydrogen atmosphere two distinct steps in coal devolatilization were observed as shown by the double peak of the devolatilization rate. Only one step was observed under nitrogen atmosphere. In a comparison of kinetic parameters, a high reaction order and a low activation energy were also obtained in the coal hydrolypyrolysis. Application of data and observations from this study could lead to a better understanding of chemical and physical changes during the coal hydrolypyrolysis and seek alternative coal conversion routes.

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Table I
COAL ANALYSIS

	Wyoming		North Dakota Lignite		Kentucky		Illinois	
	Subbituminous Coal		As		Bituminous Coal		Bituminous Coal	
	Received	Dry Basis	Received	Dry Basis	Received	Dry Basis	Received	Dry Basis
Proximate Analysis, wt%								
Moisture	6.1	--	21.2	--	3.0	--	3.9	--
Volatile	39.9	42.5	35.3	44.7	39.8	41.0	38.1	39.6
Fixed Carbon	45.6	48.6	35.9	45.6	48.6	50.1	46.8	48.7
Ash	8.4	8.9	7.6	9.7	8.6	8.9	11.2	11.7
Ultimate Analysis, wt%								
Moisture	6.1	--	21.2	--	3.0	--	3.9	--
Carbon	64.6	68.8	50.5	64.1	70.3	72.5	67.5	70.3
Hydrogen	4.3	4.6	3.5	4.4	4.8	5.0	4.5	4.7
Nitrogen	0.9	1.0	1.1	1.4	1.2	1.2	1.3	1.4
Sulfur	0.5	0.5	0.5	0.6	3.0	3.1	3.4	3.5
Ash	8.4	8.9	7.6	9.7	8.6	8.9	11.2	11.7
Oxygen (diff.)	15.1	16.1	15.6	19.7	9.1	9.4	8.2	8.4

Table II

KINETIC PARAMETERS OF COAL HYDROLYSIS^a

<u>Coal</u>	<u>Reaction Order</u>		<u>Activation Energy (kcal/mole)</u>		<u>Frequency Factor (min⁻¹)</u>	
	<u>1st Peak</u>	<u>2nd Peak</u>	<u>1st Peak</u>	<u>2nd Peak</u>	<u>1st Peak</u>	<u>2nd Peak</u>
Wyoming	2.5	3.4	18.9	64.5	1.6×10^5	1.3×10^{15}
North Dakota Lignite	2.9	4.7	23.9	70.4	4.2×10^7	1.2×10^{18}
Kentucky	2.3	--	23.4	--	3.1×10^6	--
Illinois	2.4	--	29.2	--	1.9×10^8	--

^a Samples were heated at 50°C/min under 500 psig H₂.

^b Hydrolysis characteristic peak occurred in low-rank coals.

Table III

A COMPARISON OF KINETIC PARAMETERS IN COAL PYROLYSIS

<u>Investigators</u>	<u>Coal</u>	<u>Reaction Order</u>	<u>Activation Energy (kcal/mole)</u>	<u>Frequency Factor (min⁻¹)</u>	<u>Reference</u>
Wiser et al.	Utah Bituminous	2	15.0	2.9×10^3	(9)
Stone et al.	Pittsburgh Seam Bituminous	1 ^a	27.3	3.2×10^8	(11)
Ciuryla et al.	Pittsburgh Seam Bituminous	1 ^a	39.5	1.7×10^{11}	(5)
	North Dakota Lignite	1 ^a	53.6	1.7×10^{15}	(5)
	Illinois Bituminous	1 ^a	52.3	1.7×10^{15}	(5)
Skyler et al.	Soviet Coal	2.3	10.0	1.3×10^5	(10)
	Soviet Gas Coal	2.1	14.6	5.1×10^6	(10)
This Work ^b	Wyoming Subbituminous	2.1	25.1	6.1×10^5	
	North Dakota Lignite	2.2	23.2	1.2×10^6	
	Kentucky Bituminous	1.9	26.9	4.2×10^8	
	Illinois Bituminous	1.8	30.9	4.8×10^8	

^a Based on a series of first-order reactions.

^b Samples were heated at 50°C/min under 50 cc/min ambient N₂ flow.

Table IV

KINETIC PARAMETERS OF COAL PYROLYSIS UNDER SYNGAS^a

<u>Coal</u>	<u>Reaction Order</u>		<u>Activation Energy (kcal/mole)</u>		<u>Frequency Factor (min⁻¹)</u>	
	<u>1st Peak</u>	<u>2nd Peak</u>	<u>1st Peak</u>	<u>2nd Peak</u>	<u>1st Peak</u>	<u>2nd Peak</u>
Wyoming Coal	2.8	3.6	23.1	57.5	1.1×10^7	7.1×10^{14}
North Dakota Lignite	2.6	2.8	20.8	32.6	2.6×10^6	1.8×10^{12}
Kentucky Coal	2.3	--	22.9	--	2.3×10^6	--
Illinois Coal	2.3	--	25.4	--	3.5×10^7	--

^a Samples were heated at 50°C/min under 500 psig H₂ /CO (3/1 mole ratio).

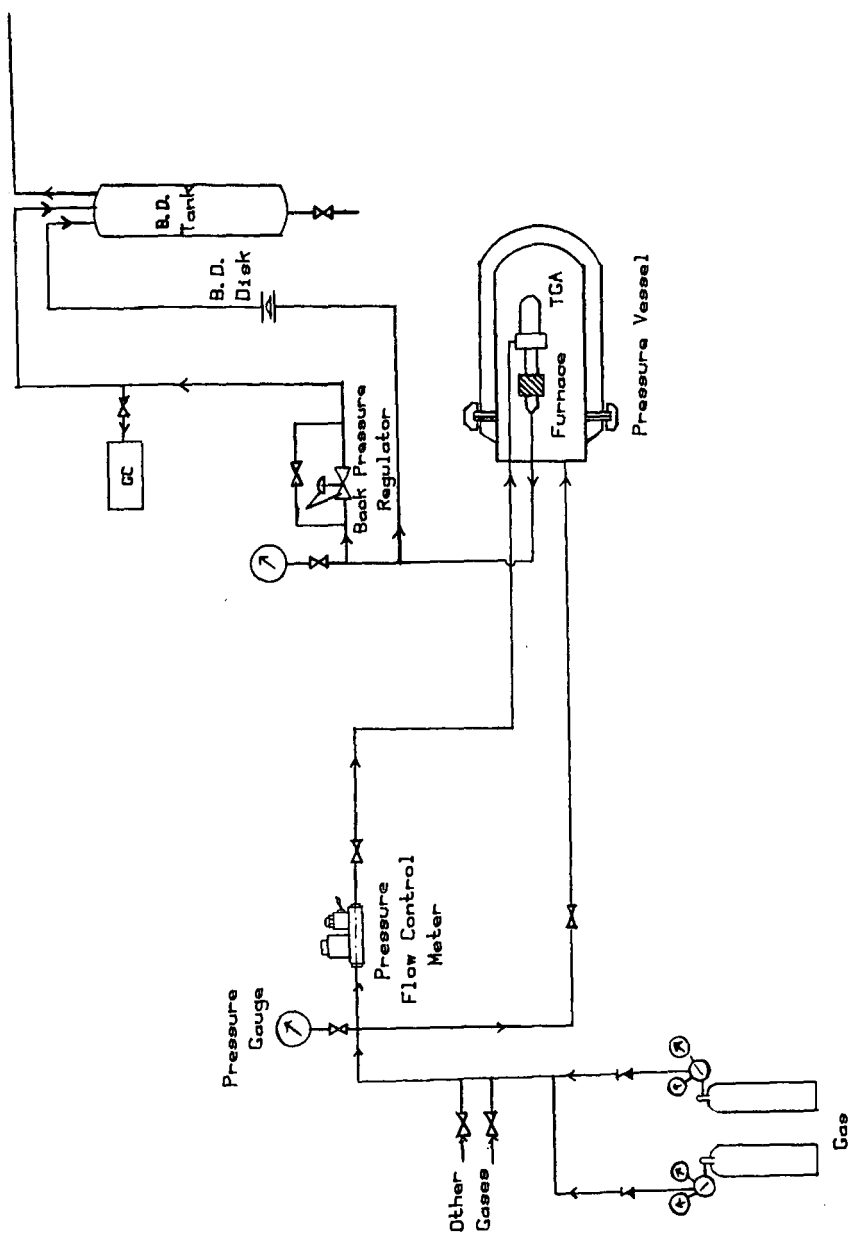


Fig. 1 Schematic Set-up of the Pressure Pyrolysis Apparatus.

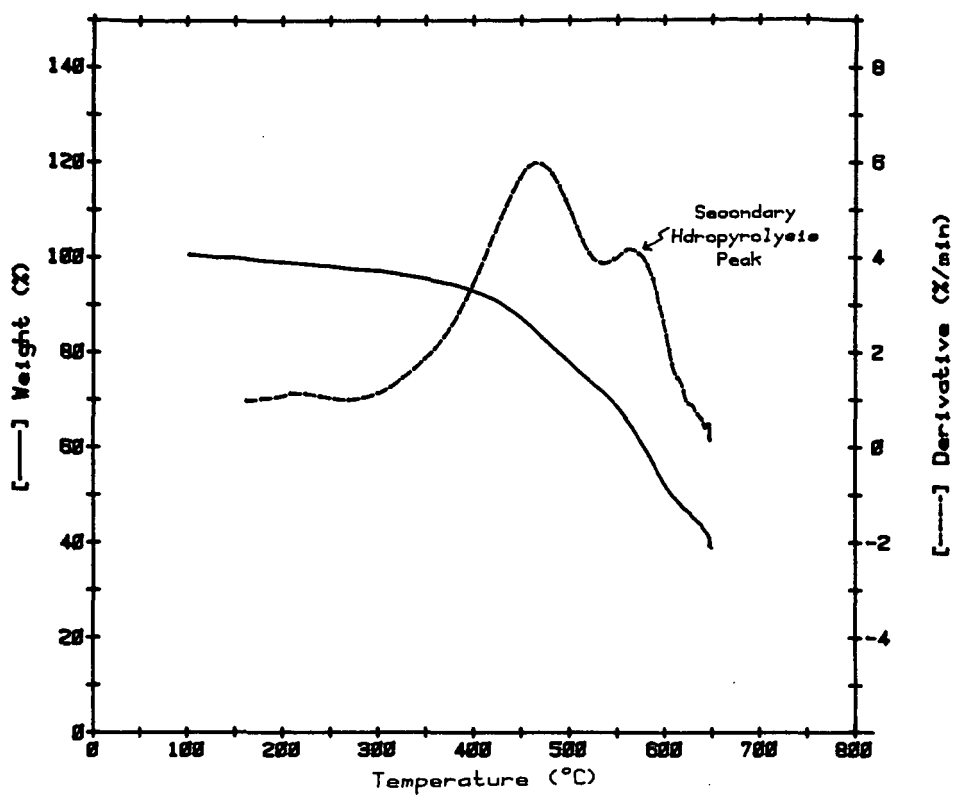


Fig. 2 Typical Pressure TGA Thermograms of Wyoming Coal Heated at 50°C/min and 500 psig H₂.

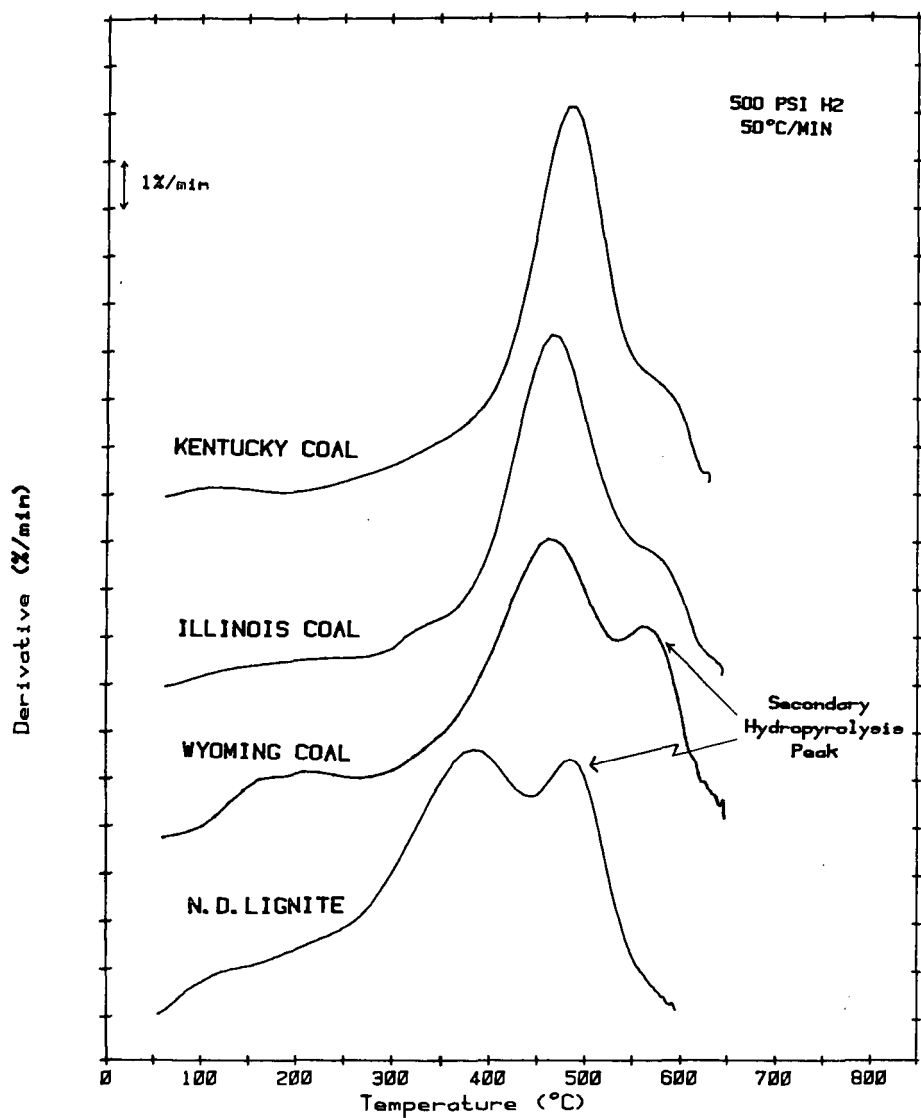


Fig. 3 A Comparison of Hydrolysis Derivative Thermograms for Various Coals at 50 °C/min and 500 psig H₂.

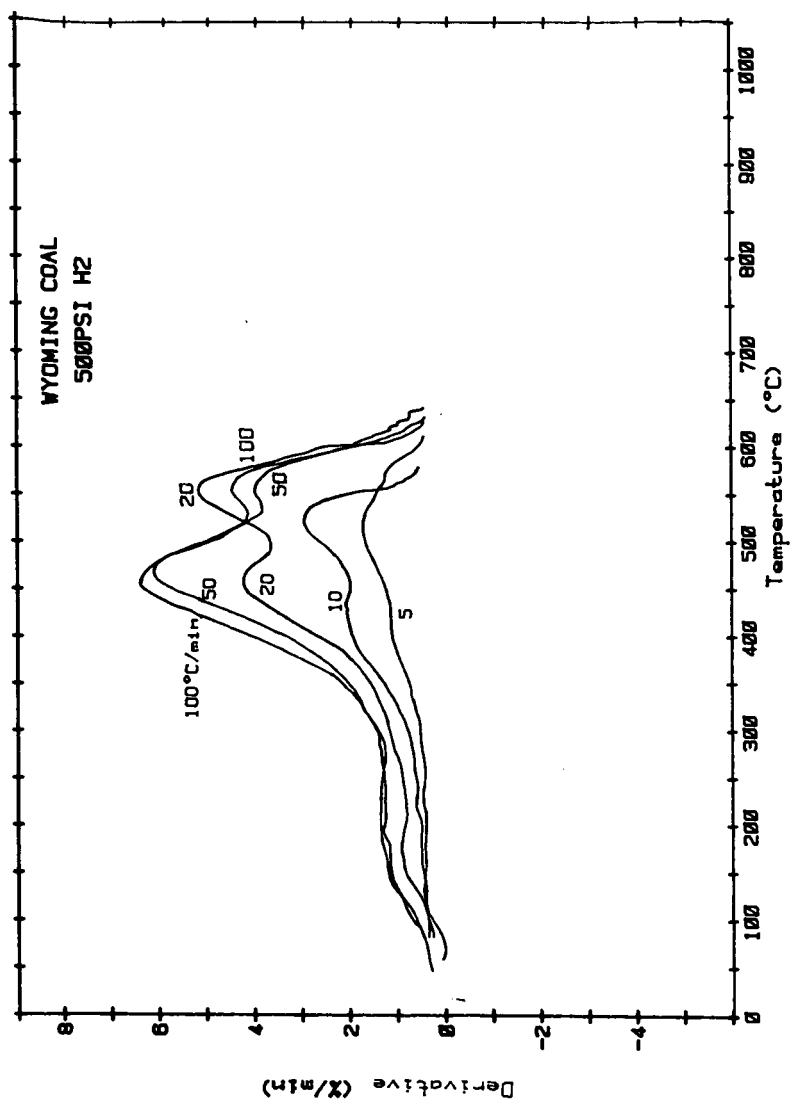


Fig. 4 The Effect of Heating Rate on Devolatilization Rate of Wyoming Coal Hydropyrolysis.

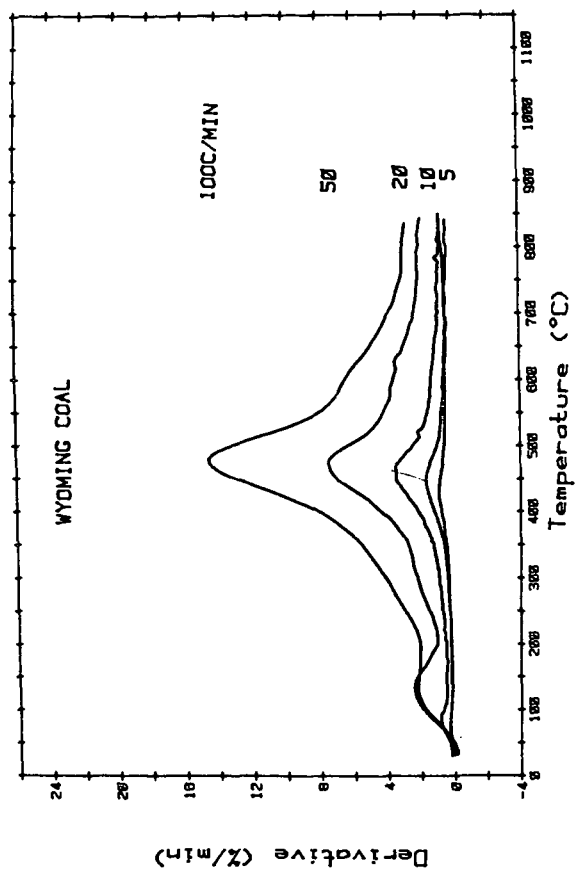


Fig. 5 Derivative Thermograms of Coal Pyrolysis at Different Heating Rates Under 1atm N₂.

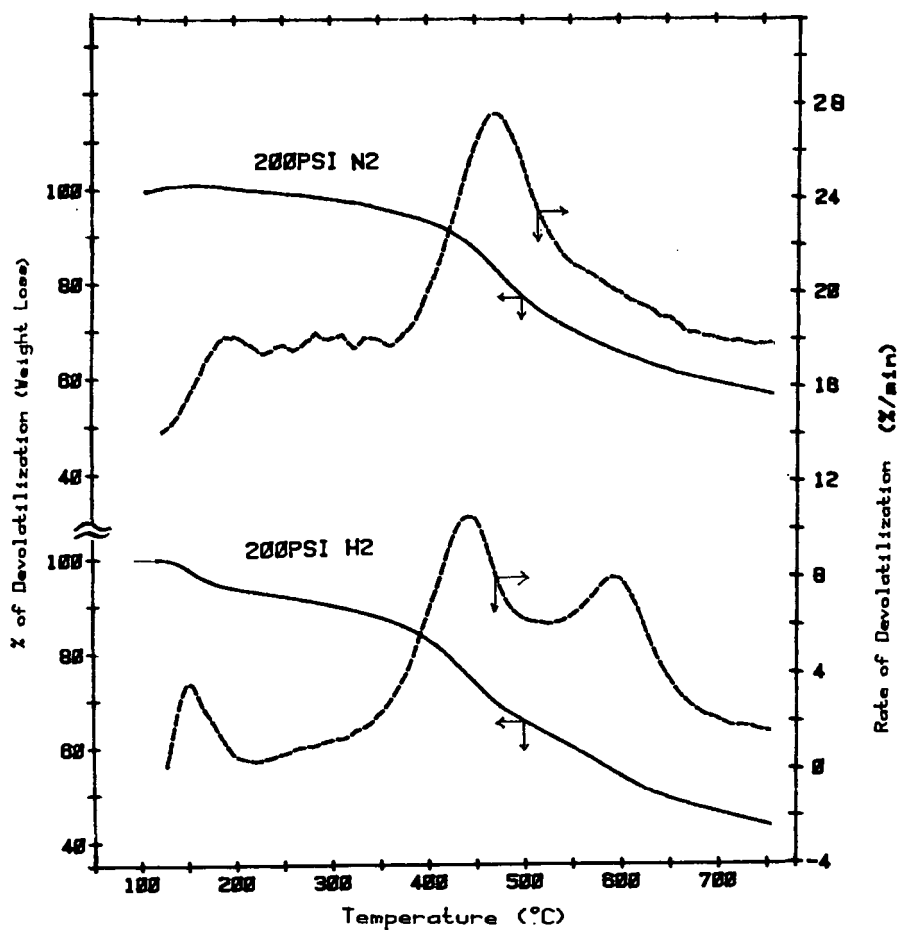


Fig. 6 A Comparison of Thermograms between Wyoming Coal Pyrolyzed in 200 psig N₂ and 200 psig H₂ at 20°C/min.

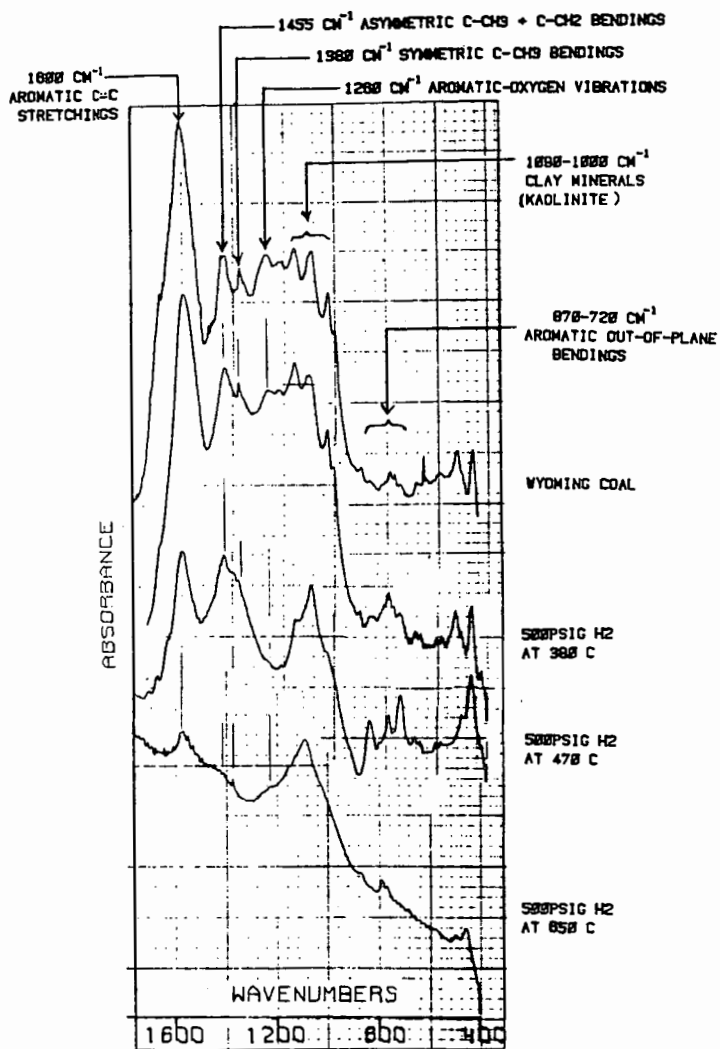


Fig. 7 FT-IR Monitor of Wyoming Coal Pyrolysis under 500 psig H₂ at Various Temperatures.

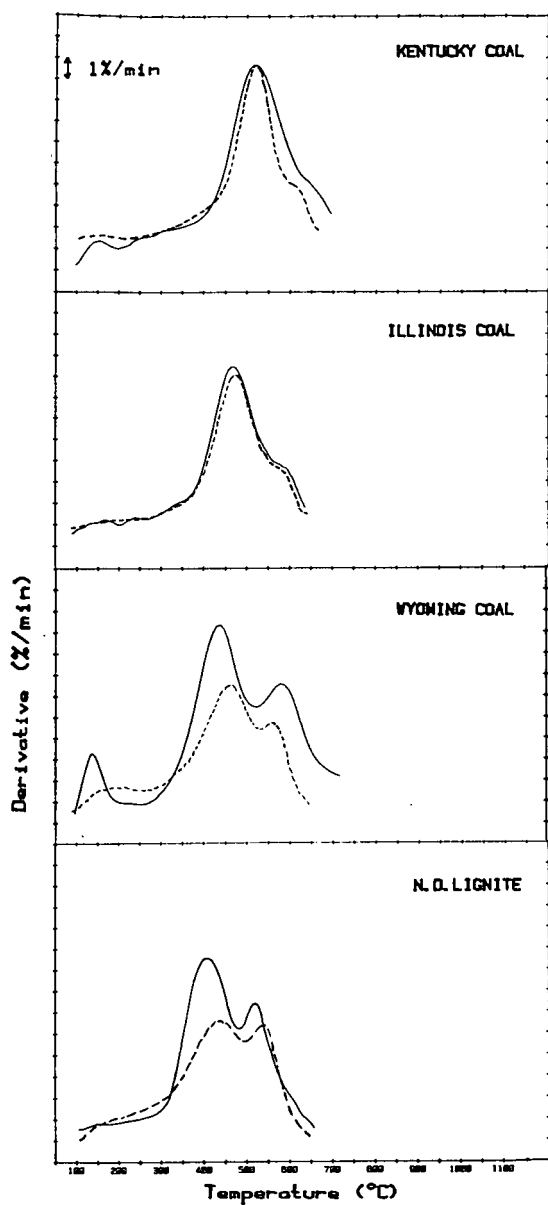


Fig. 8 The Influence of CO on Coal Devolatilization, where —; 500 psig CO/H₂ and ---; 500 psig H₂.